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Detection of Partial Discharge in SF_6 Decomposition Gas Based on Modified Carbon Nanotubes Sensors

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Abstract

Detecting and analyzing SF_6 decomposition products under partial discharge (PD) is an effective way of diagnosing the internal operating status of gas insulated switchgear (GIS). In this text, three different gas sensors are developed, whose gas-sensing materials are pure MWNTs, MWNTs modified by mixed acid and $NiCl_2$-doped MWNTs respectively. The gas sensing response for SF_6 PD decomposition products based on three MWNTs sensors is tested. The results show the mixed acid modifying could improve the sensitivity of MWNTs to detect SF_6 PD decomposition products and the doping $NiCl_2$ further improves the gas sensitivity of MWNTs, which makes MWNTs have better sensitivity and fast response characteristic.

Keywords: MWNTs; gas sensor;modification;SF_6 decomposition products; gas sensing response.

1. Introduction

Gas insulated switchgear (GIS) with sulfur hexafluoride as insulating medium has the advantages of small floor space, high-strength insulation, stable operation and so on [1-5], so it is widely applied in power system. However, inevitable insulation defects within GIS gradually extend and lead to fault. The feature of common electrical fault is manifested in insulation complete breakdown or partial discharge happening before flashover. Discharge energy can make SF_6 gas decompose, so it is possible to monitor the content of decomposition components and to forecast the level of PD, which has great significance to

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master insulation condition and to guide maintenance work of GIS. Currently, the detection methods of SF_6 discharging decomposition components mainly include gas chromatography, detector tube method, infrared absorption spectrometry and so on. It has long detection time and is not able to monitor online successively for gas chromatography; and for detector tube method, it is limited to some decomposition components and its stability is subject to high environmental impact, so the method is also inappropriate to online monitor; and for infrared absorption spectrometry, decomposition components' absorption peak is affected by SF_6, which causes the situation of cross coupling, and infrared light source has low intensity so the precision of quantitation is lacking. Gas sensor made by carbon nanotubes has the advantages of quick response, high sensitivity, low operating temperature, small size and so on, so in recent years carbon nanotubes are applied by some scholars in the sensor field, especially gas detection, which has made significant progress [6-9].

In this text, two types of modified MWNTs sensors for detecting SF_6 PD decomposition products are developed, and their properties of gas sensing response are analyzed. It is found that chemical modification and doping could change the sensitivity and fast response characteristics of MWNTs to decomposition gases.

2. The preparation for MWNTs samples and sensors

2.1. The preparation for MWNTs samples

A few MWNTs are marinated in the right amount of absolute ethyl alcohol and some surface active agent is added, which is put in the ultrasonic vibration generator and scattered in 60min. So the mixed liquor with appropriate concentration is obtained, which is regard as sample I.

Some MWNTs are marinated in the solution that is prepared by mixing concentrated sulfuric acid with concentrated nitric acid according to the volume ratio of 3:1, which is also put in the ultrasonic vibration generator and scattered in 60min. Then the solution is diluted by de-ionized water, and filtered by filtering membrane which aperture is 0.22μm. The process is repeated for several times until the solution becomes neutralized. The following process is filtering, parching and collecting MWNTs which is regard as sample II.

Next above-mentioned sample II is prepared to turbid liquid with the concentration of 2mg/ml by absolute ethyl alcohol, and 20mg $NiCl_2{\cdot}6H_2O$ is mixed into 50ml MWNTs solution. Then the solution is handled by ultrasonic vibration generator for 90min and sample III is obtained.

2.2. The preparation for MWNTs sensors

The base of the MWNTs sensor is made by printed circuit boards. Interdigital copper electrodes are etched on the base, and the thickness of copper foil is about 30μm, electrode spacing 1mm, line width 1mm, which is shown in Fig.1(a).

The preparation for MWNTs sensors without chemical modification: a few MWNTs samples I are marinated in the right amount of absolute ethyl alcohol and some surface active agent is added, which is put in the ultrasonic vibration generator and scattered. After the mixed liquor with appropriate concentration is obtained, a small amount of sample I solution with moderate concentration is put on the interdigital electrode's surface. Then the specimen is put in an oven and roasted in 80℃. The process is repeated for several times. At last the uniformly, compactly, smooth surface MWNTs membrane is prepared ,which is shown in Fig.1(b).The preparation for MWNTs sensors with chemical modification are obtained by using the same way.

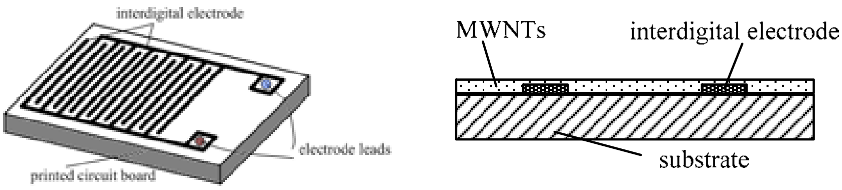

Fig.1. (a)The structure sketch of carbon nanotubes sensor before adding samples; (b)The cross section' sketch of carbon nanotubes sensor after adding samples

3. Gas sensing response test

Generating SF_6 gas discharge decomposition

The multifunctional testing apparatus of SF_6 gas decomposition products is applied for SF_6 PD decomposition experiment, as shown in Fig.2(a). Needle-plate electrode model is adopted in the experiment, and electrode spacing is 10 mm. After it is the vacuum condition in the testing apparatus, pure SF_6 gas of two atmospheric pressure is aerated into the apparatus, and 20kV voltages is exerted. PD signal waveform detected by pulse current detecting system is shown in Fig.2(b).

Gas sensing response testing

The device for MWNTs sensors detecting SF_6 PD decomposition products is shown in Fig.2(c).

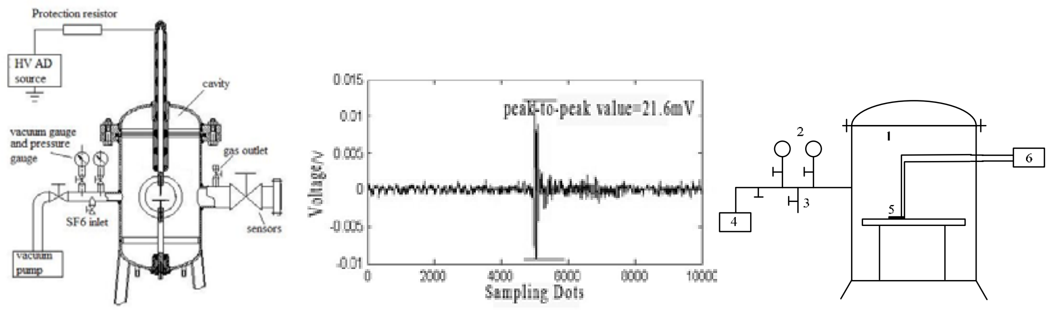

Fig.2. (a)Simulation test device of decomposition components of SF_6 gas; (b)Waveform of PD pulse under needle-plane defect; (c)Detection test device for the CNTs sensor adsorbing SF_6 decomposition products: 1. sealed metal cans 2.vacuum gauge and pressure gauge 3.air admission valve 4.vacuum air pump 5.CNTs sensor 6.impedance analyzer

After 24 hours' discharging, gas decomposition products are collected by air bags and injected through the intake valve into the detecting device with the MWNTs sensor placed inside it which is shown in Fig.2(c). At room temperature, the impedance characteristics of sensor I、II and III are respectively detected. The curves with shifted time of the resistances of sensors I, II and III are respectively shown in Fig.3 (a), (b) and (c).

It can be seen from Fig.3 that the resistor of pure MWNTs thin-film changes very small with shifted time, and the variation is about 20mΩ. The resistor of MWNTs thin-film modified by mixed acid changes largely with shifted time, and the variation reaches to 210mΩ. The resistor of $NiCl_2$-doped MWNTs thin-film changes the most obviously, and its variation is about 450mΩ.

We define the sensitivity of sensor as $S=(R-R_0)/R_0\times 100\%$, R stands for the MWNTs sensor's resistance after SF_6 PD decomposition products are injected into the detecting device and R_0 stands for the MWNTs sensor's resistance in a vacuum. From Fig.3, the sensitivities of three MWNTs sensors detecting SF_6 PD decomposition products are obtained. The results are shown in Table 1.

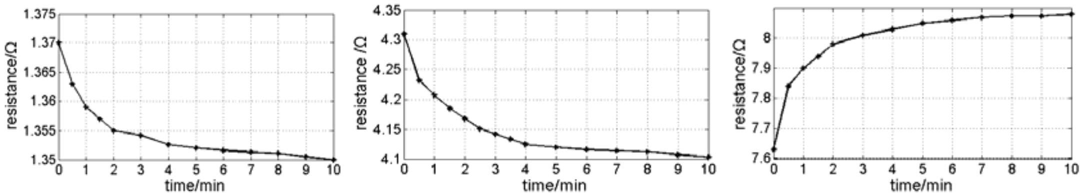

Fig.3. Variation of CNTs sensor resistance with adsorption time. (a) The curve with shifted time of the resistance of sensor I; (b) The curve with shifted time of the resistance of sensor II; (c) The curve with shifted time of the resistance of sensor III

Table 1 the sensitivities of different MWNTs sensors detecting SF_6 PD decomposition products

sensor	I	II	III
sensitivity (%)	1.5	4.81	5.90

It can be seen from Table 1, the sensitivity of pure MWNTs (sensor I) detecting SF_6 PD decomposition products is about 1.5%. The sensitivity of MWNTs modified by mixed acid (sensor II) reaches to 4.81%, and the sensitivity of $NiCl_2$-doped MWNTs has been further enhanced, which comes to 5.90%.

4. Analysis of test results

Abundant pore configurations are an important reason for MWNTs having very strong adsorbability. In Fig.3 and Table 1, it can be seen that the sensitivity of pure MWNTs (sensor I) detecting SF_6 PD decomposition products is about 1.5%, while the sensitivity of MWNTs modified by mixed acid reaches to 4.81%. After CNTs used as gas sensing layers absorb gas molecules, hybrid orbital is formed between CNTs and gas molecules, which cause its surface energy band bending, leading to charges fluctuating and transferring. So charges distribution and the concentration of charge carrieris are changed, which reflects resistance changes. The strength of gas adsorption is not only concerned with molecular characteristics, but also closely associated with gas adsorption sites. After modified by mixed acid, the length of MWNTs becomes short and the ports are open. What's more, many defects are generated at ports and their inter-outer surfaces, simultaneously large numbers of steady carboxyl, hydroxyl, carbonyl functional groups are connected at sites with defects. Therefore, on the one hand, hollow lumens and defects positions have increased, on the other hand active functional groups have grown, and more adsorption sites are provided for gases absorbed, so the sensitivity of MWNTs modified by mixed acid to SF_6 PD decomposition products is improved.

In Fig.3 and Table 1, it can be still seen that in the same experiment conditions, the sensitivity of $NiCl_2$-doped MWNTs (sensor III) reaches to 5.90%, which shows the sensitivity to SF_6 of MWNTs is improved. This may be because MWNTs, connected with functional groups, such as carboxyl, hydroxide radical, carbonyl and so on, are propitious to promote adsorption, nucleary and sediment for transitionary metal cation. At the same time, transitionary metal ions have the unique structure of hybridized orbital and the bigger charge radius, so they interact with active MWNTs functional groups easily. So after MWNTs are adulterated with Ni^{2+}, on the one hand MWNTs structure defects are aggravated, at the same time Ni^{2+} will react with gas molecules, further inducing CNTs gas-sensing membrane's surface potential barrier to change. On the other hand, the transitional metal Ni^{2+} particles in CNTs will form CNTs catalytic centre, further the gas-sensing membrane's conductivity is enhanced, and electronic transferring capability is improved. From Fig.3, we can see that the resistor of MWNTs thin-film modified by mixed acid decreased with adsorption time, while the resistor of $NiCl_2$-doped MWNTs thin-film increased. This may be because when the oxidative gas is adsorbed to the n-type semiconductor or the reducing gas is adsorbed to the p-type semiconductor, the carrier will decrease, leading to the resistance increases. Conversely, when the reducing gas is absorbed to the n-type semiconductor or the oxidative gas is absorbed to the p-type semiconductor, the carrier will increase, leading to the resistance decreased. The main decomposition products of SF_6 gas discharge include SOF_2, SO_2F_2, SO_2, SOF_4 and so on. SOF_2, SO_2F_2 and SOF_4 have strong oxidation, and SO_2 has weak reduction, so the decomposition products of SF_6 discharge mainly show oxidation. In the work environment of the atmosphere and the room temperature, pure carbon nanotubes and carbon nanotubes modified by the mixed acid show the transport properties of p-type semiconductor, so the resistance of them decrease with adsorption time. The nickel-doped carbon nanotubes are presented in the transport properties of n-type semiconductor, so the resistance of nickel-doped carbon nanotubes increase with adsorption time.

4. Conclusion

In this text, two types of modified MWNTs sensors are developed and gas sensing response for SF_6 PD decomposition products based on three types of carbon nanotubes sensors is tested. The following conclusion can be obtained: mixed acid modifying could improve the sensitivity of MWNTs to detect SF_6 PD decomposition products. The doping $NiCl_2$ further improves the gas sensitivity of MWNTs, which makes MWNTs have better sensitivity and fast response characteristic. This paper lays the foundation of researching on SF_6 PD decomposition products using MWNTs gas sensor. Through further researching and the using different chemical modification and doping, the CNTs sensor with better performance is expected to be developed to detect SF_6 PD decomposition products.

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